

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
7 October 2004 (07.10.2004)

PCT

(10) International Publication Number
WO 2004/085446 A1

(51) International Patent Classification⁷: C07F 7/12, 7/20

(21) International Application Number:
PCT/JP2004/003786

(22) International Filing Date: 19 March 2004 (19.03.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2003-081936 25 March 2003 (25.03.2003) JP

(71) Applicant (for all designated States except US): DOW
CORNING TORAY SILICONE CO., LTD. [JP/JP]; 1-3,
Marunouchi 1-chome, Chiyoda-ku, Tokyo 1000005 (JP).

(72) Inventors; and

(75) Inventors/Applicants (for US only): ONODERA,
Satoshi [JP/JP]; c/o Dow Corning Toray Silicone Co.,
Ltd., 2-2, Chigusakaigan, Ichihara-shi, Chiba 2990108
(JP). OKAWA, Tadashi [JP/JP]; c/o Dow Corning Toray
Silicone Co., Ltd., 2-2, Chigusakaigan, Ichihara-shi, Chiba
2990108 (JP).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG,
KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG,
MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH,
PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), Euro-
pean (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR,
GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR DISTILLATION OF ORGANOSILICON COMPOUNDS THAT CONTAIN ACRYLOXY OR
METHACRYLOXY GROUPS

(57) Abstract: A method for distillation of organosilicon compounds that contain acryloxy or methacryloxy groups characterized
by subjecting an organosilicon compound (A) that contains acryloxy or methacryloxy groups to distillation in the presence of a
polymerization inhibitor (B) and a compound (C) with aliphatic conjugated unsaturated bonds.



WO 2004/085446 A1

THIS PAGE BLANK (USPTO)

DESCRIPTION

METHOD FOR DISTILLATION OF ORGANOSILICON COMPOUNDS THAT
CONTAIN ACRYLOXY OR METHACRYLOXY GROUPS

5

Technical Field

[0001] The present invention relates to a method for distillation of organosilicon compounds that contain acryloxy or methacryloxy groups, and more specifically to a method for distillation of the aforementioned compounds, wherein, in spite of the fact that distillation is carried out in the presence of such inhibitors as hindered phenols or hindered-phenol precursors that have an onium-salt structure, the process proceeds without coloration, and the distillation fraction is obtained as a colorless organosilicon compound that contains acryloxy or methacryloxy groups.

15

Background Art

[0002] It is known that organosilicon compounds that contain acryloxy or methacryloxy groups react with radical-polymerizable monomers such as methylmethacrylate and styrene and are used as starting materials for copolymers obtained from the aforementioned monomers or as modifiers for the aforementioned monomers.

[0003] A method known in the art for synthesis of the aforementioned organosilicon compounds that contain acryloxy or methacryloxy groups consists of causing an addition reaction between acryloxy or methacryloxy acid esters of phenols or alcohols with aliphatic unsaturated bonds and organosilicon compounds that contain silicon-bonded hydrogen atoms, and then separating the organosilicon compounds with acryloxy or methacryloxy groups from the obtained reaction mixture by distillation. The organosilicon compounds with acryloxy or methacryloxy groups obtained by the above-described method are prone to polymerization and to an increase in the molecular weight that can easily occur during reaction of synthesis or in the step of distillation. For suppressing the undesired polymerization, radical polymerization inhibitors are generally added.

[0004] For example, Japanese Laid-Open Patent Application Publication (hereinafter referred to as "Kokai") Hei 5-186478 (equivalent to EP0520477) discloses a method with the use of N,N-dialkylaminomethylenephensols as polymerization inhibitors. Furthermore, Kokai Hei 9-295987 and Kokai Hei 9-296007 (equivalent to EP0803507), disclose processes with the use of polymerization inhibitors in the form of hindered phenols having an onium-salt structure. These inhibitors are naturally colorless and possess extremely high polymerization-inhibiting power. However, when organosilicon compounds that contain acryloxy or methacryloxy groups undergo distillation in the presence of

40

the aforementioned polymerization inhibitors, the distillation fractions are subject to coloration, and it becomes very difficult to obtain colorless distillation fractions of high purity.

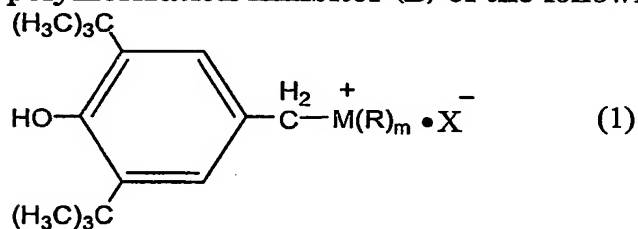
- 5 [0005] Kokai Sho 48-85501 (equivalent to US3801615) discloses a method for decoloration of benzoquinone, which is a coloring component, by adding an olefinic unsaturated conjugated diene to oxidation-polymerizable monoolefinic unsaturated monomer synthesized by distillation with the use of hydroquinone as an inhibitor. However, the use of hindered phenols in the above method as
 10 polymerization inhibitors cannot prevent coloration of the distillation fractions. this occurs, probably, because the benzoquinone and the coloring substance admixed with the distillation fraction have different structures.

- 15 [0006] It is an object of the present invention to provide a method for inhibiting coloration of products of distillation of organosilicon compounds with acryloxy or methacryloxy groups when the distillation is carried in the presence of polymerization inhibitors in the form of hindered phenols having an onium-salt structure or their hindered phenol precursors.

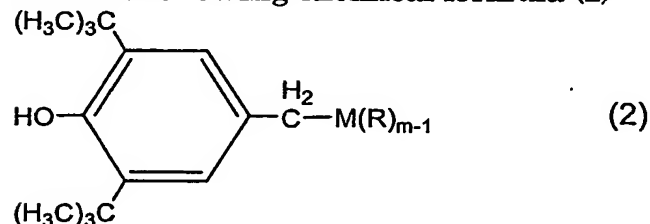
20

Disclosure of Invention

- [0007] The present invention relates to a method for distillation of organosilicon compounds that contain acryloxy or methacryloxy groups characterized by subjecting an organosilicon compound (A) that contains
 25 acryloxy or methacryloxy groups to distillation in the presence of a polymerization inhibitor (B) of the following general formula (1):



or of the following chemical formula (2):



- 30 (where, M is an atom selected from the group consisting of N, P, As, Sb, O, S, Se, Sn and I; R is a monovalent hydrocarbon group or a hydrogen atom; m is 1, 2 or 3; and X is a conjugated base of an organic acid or inorganic acid) and a compound (C) with aliphatic conjugated unsaturated bonds.

Best Mode for Carrying Out the Invention

[0008] The invention will be further described in more detail.

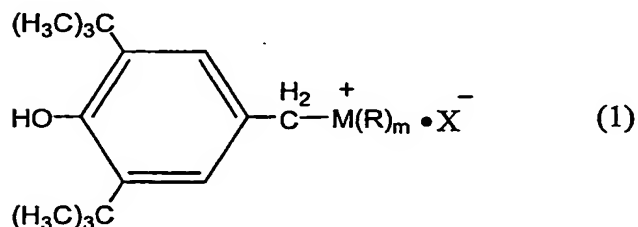
[0009] There are no special restrictions with regard to the structure of the organosilicon compound (A) that contains acryloxy or methacryloxy groups, except that it should contain acryloxy or methacryloxy groups and should have a boiling point that provides isolation under the effect of distillation.

[0010] The following are examples of the aforementioned organosilicon compound: 3-methacryloxypropyl-dimethylchlorosilane, 3-methacryloxypropyl-methyldichlorosilane, 3-methacryloxypropyl-trichlorosilane or similar chlorosilanes that contain methacryloxy groups; 3-acryloxypropyl-dimethylchlorosilane, 3-acryloxypropylmethyl-dichlorosilane, 3-acryloxypropyl-trichlorosilane, or similar chlorosilanes that contain acryloxy groups; 3-methacryloxypropyl-dimethylmethoxysilane, 3-methacryloxypropyl-methyldimethoxysilane, 3-methacryloxypropyl-trimethoxysilane, 3-methacryloxypropyl-dimethylethoxysilane, 3-methacryloxypropyl-methyldiethoxysilane, 3-methacryloxypropyl-triethoxysilane, or similar alkoxysilanes that contain methacryloxy groups; 3-acryloxypropyl-dimethylmethoxysilane, 3-acryloxypropylmethyl-dimethoxysilane, 3-acryloxypropyl-trimethoxysilane, 3-acryloxypropyl-dimethylethoxysilane, 3-acryloxypropyl-methyldiethoxysilane, 3-acryloxypropyl-triethoxysilane or similar alkoxysilanes that contain acryloxy groups; 1,3-bis (methacryloxypropyl) tetramethyldisiloxane, (methacryloxypropyl) pentamethyldisiloxane, methacryloxypropyl- tris (trimethylsiloxy) silane or similar siloxane oligomers that contain methacryloxy groups; 1,3-bis (acryloxypropyl) tetramethyldisiloxane, acryloxypropyl-pentamethyldisiloxane, acryloxypropyl tris (trimethylsiloxy) silane or similar siloxane oligomers that contain acryloxy groups.

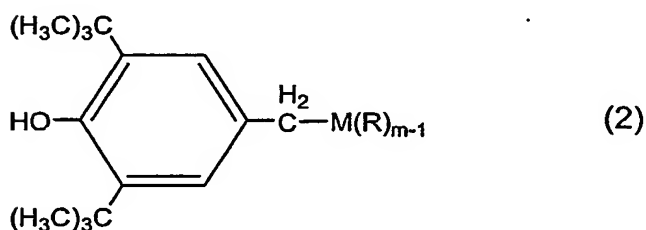
[0011] Component (A) can be synthesized by a known method which is described, e.g., in Kokai 5-186478 and Kokai 9-295987. According to an appropriate method, an acrylic or methacrylic acid ester of phenol or an alcohol with aliphatic unsaturated bonds and alkoxysilane or chlorosilane with silicon-bonded hydrogen atoms are subjected to a hydrosilation reaction in the presence of component (B). Furthermore, for obtaining siloxane oligomers that contain acryloxy or methacryloxy groups, low-molecular-weight alkoxysilanes or chlorosilanes with acryloxy or methacryloxy groups can be either subjected to hydrolysis and condensation, or caused to react with linear-chain, cyclic, or branched organosiloxane oligomers in the presence of an acidic catalyst.

[0012] A polymerization inhibitor that constitutes component (B) is intended for inhibiting polymerization and increase in molecular weight during synthesis

and/or distillation of aforementioned component (A). Component (B) can be represented by hindered phenols expressed by the following general formulae:



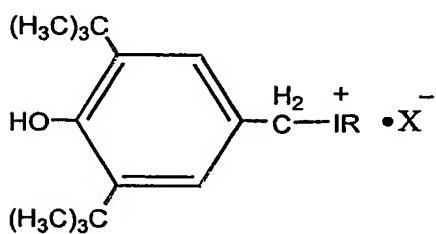
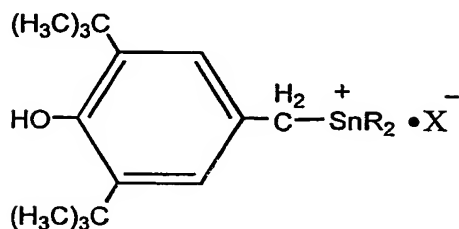
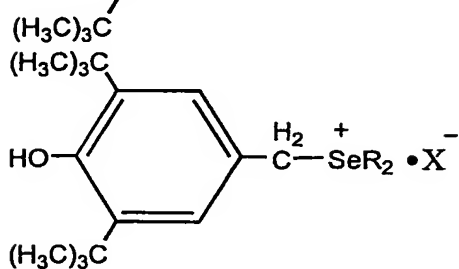
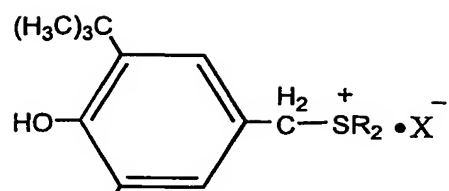
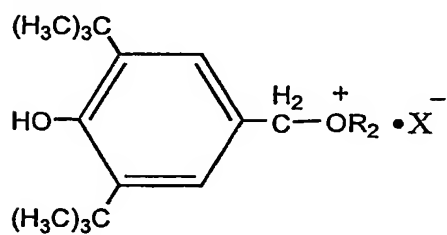
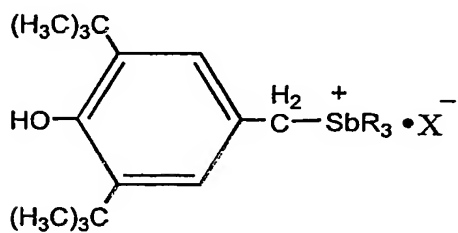
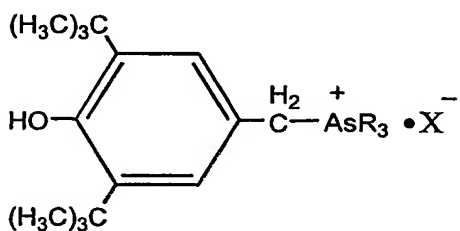
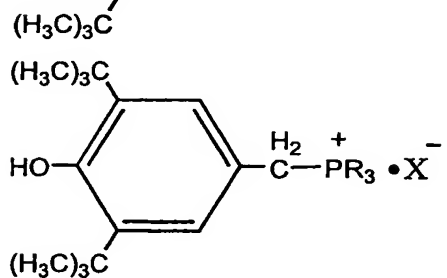
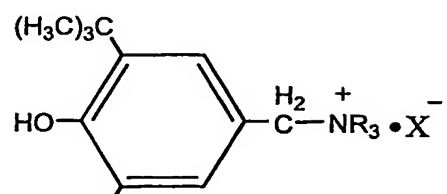
or,



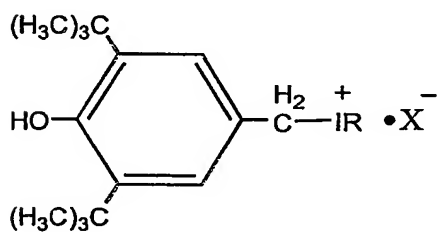
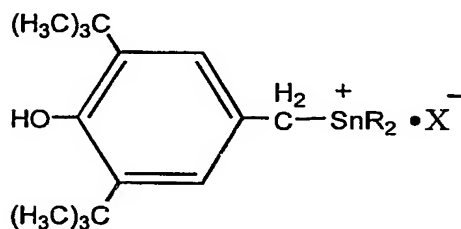
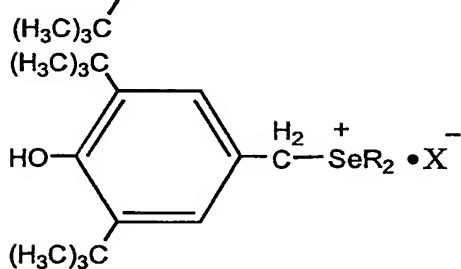
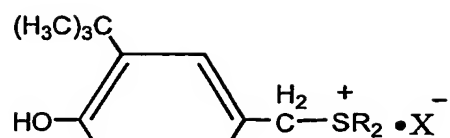
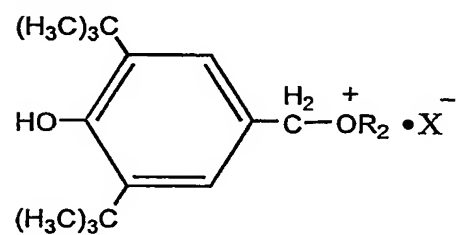
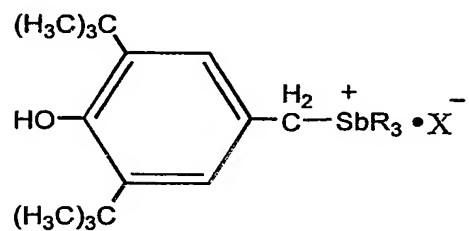
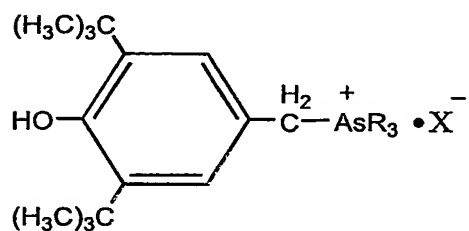
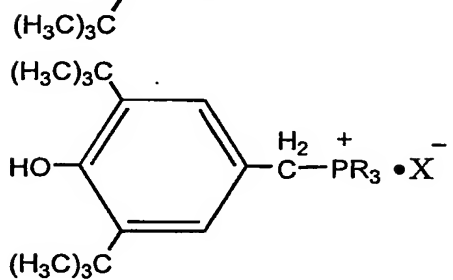
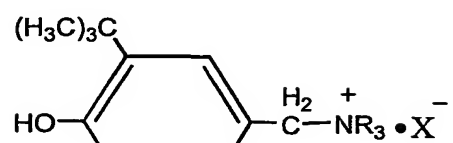
(where, M is an atom selected from the group consisting of N, P, As, Sb, O, S, Se, Sn and I; R is a univalent hydrocarbon group or hydrogen atom; m is 1, 2 or 3; X is a conjugated base of an organic or inorganic acid). In the above formula, R may designate a hydrogen atom or a univalent hydrocarbon group such as methyl group, ethyl group, propyl group, or a similar alkyl group; vinyl group, allyl group, butenyl group, or a similar alkenyl group; phenyl group, tolyl group, xylyl group, or a similar aryl group; phenethyl group, diphenylmethyl group, or a similar aralkyl group. Of these, most preferable are alkyl group or hydrogen atoms, especially alkyl groups and hydrogen atoms. In the above formula, M may designate an atom selected from the group consisting of N, P, As, Sb, O, S, Se, Sn and I; m may be 1, 2 or 3, but when M is N, P, As, or Sb, m is 3, when M is O, S, Se, or Sn, m is 2, and when M is I, m is 1. X designates a conjugated base of an organic or inorganic acid and may comprise a halide ion in the form of a conjugated base of hydrogen chloride, hydrogen bromide, or the like, a conjugated base of acetic acid, propionic acid, acrylic acid, or a similar carboxylic acid, as well as a conjugated base of a sulfonic acid or phosphoric acid.

[0013] Appropriate compounds are exemplified by the following chemical structures, where R and X are the same as defined above:

[0014]

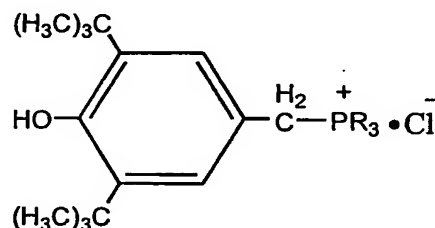
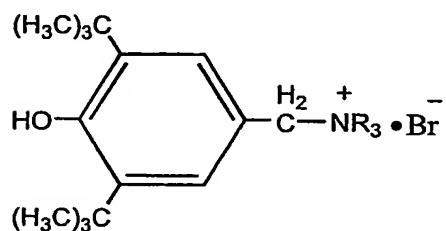
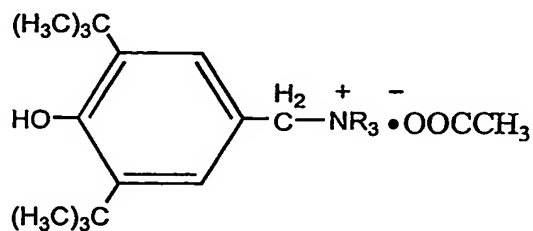
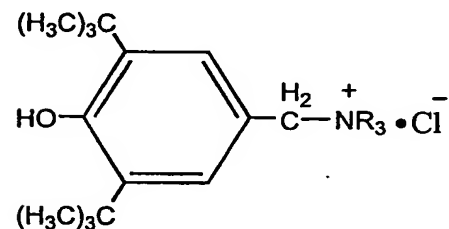


[0015]



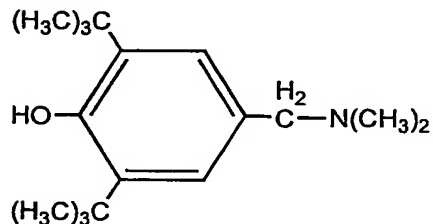
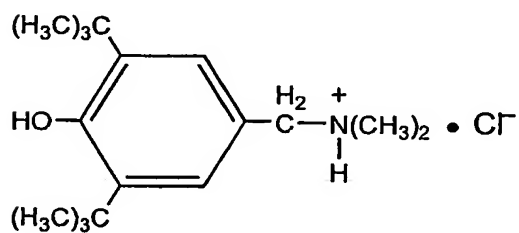
[0016] Component (B) may have chemical structures shown above, of which those given below are most preferable (in the following formulae R designates hydrogen atom or the same univalent hydrocarbon group as defined above).

5 [0017]



10 [0018] Those of the aforementioned compounds that comprise hindered phenols with an onium salt structure can be easily synthesized by a known method that consists of reacting hindered phenols, having an appropriate Lewis base structure, with an organic or inorganic acid or an organic halide.

[0019] The following compounds are most suitable for component (B) from the point of view of availability and ease of synthesis:



[0020] An effective amount of component (B) that should be added to the process depends on conditions of the synthesis reaction and distillation, but, in general, the added amount should be within the range of 0.001 wt.% to 10 wt.%.

5 [0021] A compound with aliphatic conjugated unsaturated bonds that constitutes component (C) is intended for capturing coloring components generated in the aforementioned component (B) with its conjugated unsaturated bonds, and forming into adducts with a high boiling point, and are not admixed with the distillation fractions.

10 [0022] The following are examples of compounds suitable for use as component (C): butadiene, piperylene, isoprene, cyclopentadiene, 2-phenylbutadiene, bicyclohexene, 2,3-dimethylbutadiene, 1,3-cyclohexadiene, 1-phenylbutadiene, 9,10-dimethylanthracene, 1,2-dimethylenecyclohexane, 1,2-
15 diethylenecyclohexene, 1-methoxybutadiene, 1,1'-bicyclopentene, conjugated linolic acid, dehydrated castor oil, or similar conjugated diene-structure compounds; alloocimene, tung oil, α -eleostearic acid or a similar conjugated triene-structure compound; cyclooctatetraene, or a similar conjugated tetraene-structure compound.

20 [0023] In some distilling condition, if the adduct with a coloring substance and component (C) have low boiling points, it would be impossible to obtain a colorless fraction of distillation due to contamination of them with distillation fraction depending upon distillation conditions, and therefore it is necessary to
25 provide component (C) with as high boiling point as possible. From this point of view, it is recommended to use a conjugated linolic acid, dehydrated castor oil, tung oil, α -eleostearic acid, and cyclooctatetraene. Of these, α -eleostearic acid, and cyclooctatetraene are most preferable as they have conjugated triene structures or conjugated tetraene structures highly reactive with coloring
30 substances, while a tung oil is most preferable from the point of view of availability.

[0024] It is recommended to use component (C) in an excess of the amount only needed for obtaining a colorless fraction. The minimal amount required for the
35 process will depend on many factors, such as the quantity and chemical structure required for the target organosilicon compound with acryloxy or methacryloxy groups, the boiling point, the quantity and the boiling point required for the target compound, as well as on the chemicals structure, boiling point, and other characteristics of component (C) itself. In general, however, component (C)
40 should be used in an amount from 0.1 wt. % to 3000 wt. % relative to the weight of component (B).

[0025] During distillation, component (C) can be used alone
45 or in combination with inorganic powders, glass beads, carbon black or other substances that can absorb (C) on their surfaces or fix component (C) with a

chemical bond on their surfaces. In the last-mentioned case, component (C) can be represented by a lower-melting-point compound. If component (C) is fixed with chemical modification on the surface of such additives, it is required that the residual group contain aliphatic conjugated unsaturated bonds.

[0026] It is recommended that distillation of component (A) be conducted under low pressure and at a temperature as low as possible. This is because the above condition facilitates suppression of polymerization and increase in molecular weight, allows for decrease in the amount of the added polymerization inhibitor, and allows for decrease in the amount of coloring substance formed during distillation. For example, distillation can be carried out under pressure below 3000 Pa, preferably below 1500 Pa, and at a temperature between 80 and 150 °C, preferably between 100 and 130 °C.

[0027] In the distillation process, polymerization and increase in the molecular weight of component (A) may be further inhibited by additionally compounding components (B) and (C) with metal halides disclosed in Kokai 5-271248. Such a metal halide may comprise, e.g., copper chloride. Other additives may comprise known antioxidants such as hindered phenol compounds (except for component (B)), amine-type compounds, quinone-type compounds, or the like. Of these, most preferable are hindered phenols (except for component (B)). Although there are no restrictions with regard to the amounts in which the aforementioned antioxidants can be used, it is recommended that their amount in the reaction mixtures with component (A) be within the range of 0.1-10 wt. %. The use of copper chloride and antioxidants is especially advantageous when component (A) is represented by 3-methacryloxypropyl-dimethylchlorosilane.

[0028] In spite of the fact that normally the use of onium-structured hindered phenols and their precursors that possess strong polymerization inhibiting capacity is accompanied by coloration of distillation fractions, the distillation method of the invention makes it possible to obtain organosilicon compounds with acryloxy and methacryloxy groups which are colorless even with the use of the aforementioned high-capacity inhibitors. Since the organosilicon compounds with acryloxy and methacryloxy groups obtained by the method of the invention are colorless, by reacting them with radical-polymerizable monomers, it is possible to prepare starting material for copolymers that can be derived from such monomers or to prepare modifiers for polymers obtained from the aforementioned monomers. In other words, the aforementioned organopolysiloxanes may find application in the fields of industry that requires optically colorless properties.

[0029] Examples

The invention will be further described with reference to application examples. In order to quantitatively evaluate the color of the fractions obtained after distillation, the light absorbance of the fractions was measured with the use of

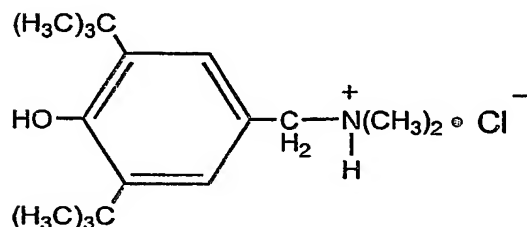
an UV spectro photometer at a wavelength of 350 nm. In observation with the naked eye, the fraction with absorbance below 0.055 at 350 nm wavelength was seen as completely colorless.

5 [0030] Reference Example 1

[Preparation of Hydrochloride of N,N-Dialkylaminomethylenephenol]

A transparent liquid solution was prepared by mixing 1 g (3.8 mmol) of 2,6-di-t-butyl-4-dimethylaminomethylphenol, 0.76 g (8.4 mmol) of trimethylsilanol and 30 ml of toluene. While the mixture was stirred, 0.46 g (4.2 mmol) of trimethylchlorosilane were added to the mixture dropwise, whereby a white precipitate was formed. The product was stirred for 30 min. at room temperature, and the white precipitate was separated by filtering. The obtained white precipitate was washed with toluene and then dried in vacuum for 1 hour at 80 °C. The weight of the obtained white precipitate was 0.7 g.

15 Nuclear magnetic resonance (NMR) analysis and infra-red (IR) light-absorption analysis of the white precipitate showed that it was hydrochloride of 2,6-di-t-butyl-4-dimethylaminomethylenephenol having the following chemical structure:



20 [0031] Reference Example 2

[Synthesis of Methacryloxypropyl Dimethylchlorosilane]

A four-neck flask equipped with a stirrer was loaded with 1000 g (7.92 mole) of allyl methacrylate (AMA) (the product of Mitsubishi Gas Chemical Co., Ltd.) and 1.5 g of the hydrochloride of 2,6-di-t-butyl-4-dimethylaminomethylenephenol prepared in aforementioned Reference Example 1. The mixture was then combined and further mixed with a complex of platinum and 1,3-divinyltetramethyldisiloxane (the content of metallic platinum was 20 ppm per total weight of the allyl methacrylate and dimethylchlorosilane). While the mixture was stirred and heated at 80 °C, a small amount of dimethylchlorosilane was added dropwise. After verification of the fact that reaction has been initiated, the reaction system was cooled by water or by air, and the temperature was maintained within the range of 65-75 °C, 682 g (7.2 mole) while dimethylchlorosilane were added dropwise. When the addition process was over, the product was stirred for 1 hour at 70 °C. A small sample was taken from the reaction mixture. The area percent of the gas chromatography (GLC) peak of obtained methacryloxypropyl dimethylchlorosilane was 70 %.

[0032] Application Example 1

A four-neck flask equipped with a stirrer was loaded with 400 g of the reaction mixture obtained in Reference Example 2, 0.2 g of 2,6-di-*t*-butyl-4-methylphenol, 4 g of Copper(II) chloride, anhydrous and 4 g of tung oil (the product of Kimura Shoji), and the mixture was subjected to distillation in a 10 cm-long Vigreux column under a reduced pressure of 1330 Pa. The residue comprised 50 g of a low-viscosity brown liquid. 190 g of the 110-120 °C distillation fraction was sampled. Gas chromatography analysis of the sample showed that the obtained colorless fraction comprised 3-methacryloxypropyl-dimethylchlorosilane. GLC purity of the product was 97.0 %. Absorbance of the obtained 3-methacryloxypropyl-dimethylchlorosilane measured at 350 nm was 0.028.

[0033] Application Example 2

Distillation was carried out under the same conditions as in Application Example 1, with the exception that the tung oil was replaced by the same quantity of a linolic acid (the product of KF TRADING Co., LTD, tradename Hy-Diene). The residue comprised 56 g of a low-viscosity brown liquid. 198 g of the obtained colorless distillation fraction was analyzed by gas chromatography analysis that showed that the product comprised 3-methacryloxypropyl-dimethylchlorosilane. GLC purity of the product was 97.1 %. Absorbance of the obtained 3-methacryloxypropyl dimethylchlorosilane measured at 350 nm was 0.042.

[0034] Application Example 3

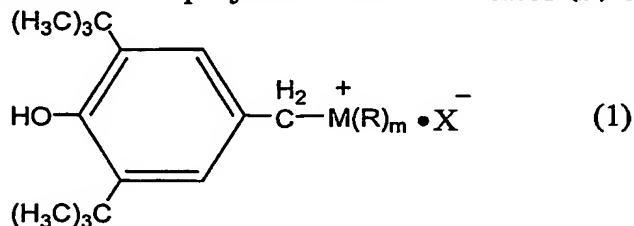
Distillation was carried out under the same conditions as in Application Example 1, with the exception that the tung oil was replaced by the same quantity of a dehydrated castor oil (the product of KF TRADING Co., LTD, tradename Dassui Himashiyu [Dehydrated Castor Oil]). The residue comprised 64 g of a low-viscous brown liquid. 198 g of the obtained colorless distillation fraction was analyzed by gas chromatography analysis that showed that the product comprised 3-methacryloxypropyl-dimethylchlorosilane. GLC purity of the product was 97.1 %. Absorbance of the obtained 3-methacryloxypropyl dimethylchlorosilane measured at 350 nm was 0.030.

[0035] Comparative Example 1

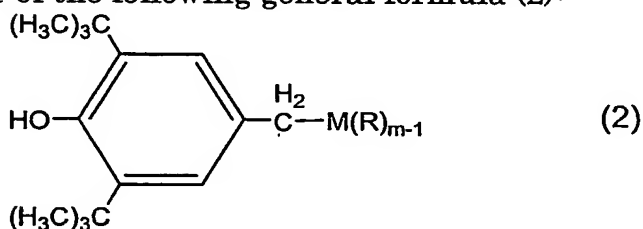
Distillation was carried out under the same conditions as in Application Example 1, but without the use of the tung oil. The residue comprised 82 g of a low-viscosity brown liquid. 214 g of the obtained distillation fraction was analyzed by gas chromatography analysis that showed that the product comprised 3-methacryloxypropyl dimethylchlorosilane. GLC purity of the product was 97.5 %. However, the fraction had a yellow color. Absorbance of the obtained 3-methacryloxypropyl dimethylchlorosilane measured at 350 nm was 0.060.

CLAIMS

1. A method for distillation of organosilicon compounds that contain acryloxy or methacryloxy groups characterized by subjecting an organosilicon compound (A) that contains acryloxy or methacryloxy groups to distillation in the presence of a polymerization inhibitor (B) of the following general formula (1):

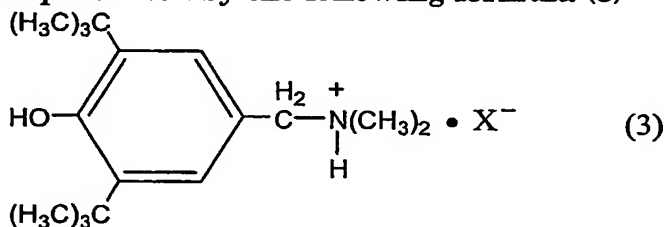


or of the following general formula (2):

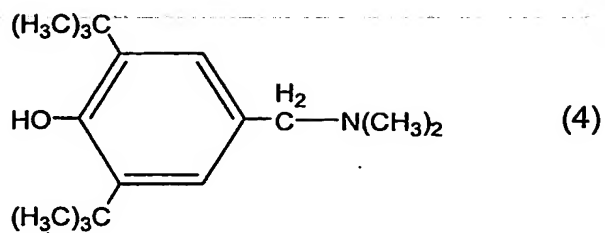


(where M is an atom selected from the group consisting of N, P, As, Sb, O, S, Se, Sn and I; R is a monovalent hydrocarbon group or a hydrogen atom; m is 1, 2 or 3; and X is a conjugated base of an organic acid or inorganic acid) and a compound (C) with aliphatic conjugated unsaturated bonds.

2. The method of distillation according to Claim 1, wherein said component (B) is a polymerization inhibitor in which M of formula (1) is nitrogen atom.
3. The method of distillation according to Claim 1, wherein said component (B) is represented by the following formula (3):



or by the following formula (4):



4. The method of distillation according to any of Claims 1 to 3, wherein said component (C) is selected from the group consisting of a conjugated linolic acid, dehydrated castor oil, tung oil, α -eleostearic acid, and cyclooctatetraene.
5. The method of distillation according to Claim 1, wherein said component (A) is 3-methacryloxypropyl-dimethylchlorosilane.
6. The method of distillation according to Claim 1 or Claim 5, wherein distillation is carried out in the presence of copper chloride.
7. The method of distillation according to Claim 6, wherein distillation is carried out in the presence of an antioxidant selected from the group consisting of a hindered phenol compound (with the exception of said component (B)), an amine-type compound, and a quinone-type compound.

THIS PAGE BLANK (USPTO)

INTERNATIONAL SEARCH REPORT

national Application No

TCT/JP2004/003786

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F7/12 C07F7/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	DE 102 49 637 C (WACKER CHEMIE GMBH) 18 December 2003 (2003-12-18) the whole document	1-7
A	EP 0 803 507 A (DOW CORNING TORAY SILICONE) 29 October 1997 (1997-10-29) cited in the application the whole document	1-7
A	EP 0 520 477 A (UNION CARBIDE CHEM PLASTIC) 30 December 1992 (1992-12-30) cited in the application claim 6	1-7
A	US 3 801 615 A (CHUANG V) 2 April 1974 (1974-04-02) cited in the application claims	1-7
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

15 July 2004

Date of mailing of the international search report

27/07/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Elliott, A

INTERNATIONAL SEARCH REPORT

national Application No

PCT/JP2004/003786

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 562 584 A (DOW CORNING TORAY SILICONE) 29 September 1993 (1993-09-29) the whole document -----	1,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

CT/JP2004/003786

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 10249637	C	18-12-2003	DE 10249637 C1	18-12-2003
EP 0803507	A	29-10-1997	JP 9296007 A	18-11-1997
			JP 9295987 A	18-11-1997
			EP 0803507 A2	29-10-1997
			US 5914418 A	22-06-1999
			US 5723643 A	03-03-1998
EP 0520477	A	30-12-1992	US 5103032 A	07-04-1992
			CA 2072547 A1	28-12-1992
			DE 69217736 D1	10-04-1997
			DE 69217736 T2	12-06-1997
			EP 0520477 A1	30-12-1992
			JP 2663081 B2	15-10-1997
			JP 5186478 A	27-07-1993
US 3801615	A	02-04-1974	AU 5130773 A	25-07-1974
			CA 1002058 A1	21-12-1976
			DE 2304735 A1	09-08-1973
			FR 2170101 A1	14-09-1973
			GB 1417454 A	10-12-1975
			JP 980522 C	18-12-1979
			JP 48085501 A	13-11-1973
			JP 54014082 B	05-06-1979
EP 0562584	A	29-09-1993	JP 2851477 B2	27-01-1999
			JP 5271248 A	19-10-1993
			DE 69311183 D1	10-07-1997
			DE 69311183 T2	09-10-1997
			EP 0562584 A1	29-09-1993
			US 5262555 A	16-11-1993

THIS PAGE BLANK (USPTO)